



Catalytic ozonation for the removal of organic contaminants in water on ZSM-5 zeolites



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ABSTRACT

The results presented in this study aim to show the potential of ozonation of common water pollutants (volatile organic chemicals, pharmaceuticals and carboxylic acids, ozonation by-products) on ZSM-5 zeolites and to investigate the effect of the nature of pollutants on the efficiency of catalytic ozonation. Both the H-ZSM-5 and Na-ZSM-5 forms with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and counter ions ($\text{Z1000H}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 1000$, $\text{Z900Na}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$, $\text{Z25H}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ and $\text{Z25Na}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) have been used. The effects of pH, adsorption, presence of hydroxyl radical scavengers, phosphates and humic acids on the efficiency of catalytic ozonation have been investigated. The results revealed that catalytic ozonation on zeolites could substantially enhance the removal of VOCs and ibuprofen when compared with ozonation alone and that adsorption plays a key role in the effectiveness of this process. Zeolites with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were found to have a high adsorption capacity towards VOCs and as a result high catalytic activity. On the other hand zeolites with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios had a high adsorption capacity towards ibuprofen in its ionised form. Catalytic processes have been found to be pH dependent with the highest activity at acidic pH. The presence of hydroxyl radical scavengers (phosphates and humic acid) did not have a significant effect on the removal of contaminants on ZSM-5 zeolites. Despite high activity towards VOCs and ibuprofen, zeolites did not catalyse the removal of acetic acid in water at studied pH values. It is therefore suggested that catalytic ozonation of organic pollutants on ZSM-5 zeolites proceeds via direct reactions of molecular ozone with pollutants adsorbed on the surface of zeolites.

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1. Introduction

Heterogeneous catalytic ozonation has been applied in the degradation of organic compounds such as pharmaceuticals, pesticides, dyes, aromatic hydrocarbons and organic acids etc. Among effective catalysts of the ozonation process are: activated carbons [1], Al_2O_3 [2] and TiO_2 [3]. Advanced oxidation processes involve the production of hydroxyl radicals. However, their reactions are not selective and therefore more likely to be hindered by competitive reactions. Therefore, it is important to investigate new methods utilising molecular ozone reactions. Among the non-polar materials that have been investigated are: perfluorinated alumina [4], high silica zeolites [5] and perfluorinated MCM-41 [6]. Ozonation on perfluorinated alumina showed high degradation efficiency of ethers [7], hydrocarbons [8] and natural organic matter [2,6] in water.

ZSM-5 zeolites were also found to act as effective catalysts of molecular ozone reactions [9] with several organic compounds such as trichloroethene [5] and phenol [10]. Therefore, applications of materials such as ZSM-5 zeolites as heterogeneous catalysts of oxidation of common water micro-pollutants are desirable and should be investigated further. Additionally, it is important to understand mechanisms of ZSM-5 zeolites and to study the effect of different types of pollutants on catalytic process utilising ZSM-5 zeolites. The aim of this work is (i) to verify the activity of zeolites as catalysts of ozonation of three different types of organic pollutants (VOCs, pharmaceuticals and carboxylic acids) in water as well as (ii) to further understanding of mechanisms of catalytic ozonation on zeolites of different types of pollutants.

The first group of studied pollutants is represented by VOCs, which are an important class of priority pollutants. They have been detected in drinking water [11]. The chlorinated aromatic compounds are a class of highly toxic and widely used organic pollutants that are highly resistant to ozonation [12]. Therefore, catalytic ozonation, which has already been successfully used for the removal of VOCs from both aqueous media [13,14] and air [15,16],

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could be considered as a viable solution for the effective removal of these pollutants from.

Pharmaceuticals are emerging pollutants. Although they are present in trace amounts in the aquatic environment, long term exposure to these compounds poses a potential risk to aquatic life and humans, as pharmaceuticals have been detected in drinking water [17]. In recent years ozonation [18] and advanced oxidation processes [19,20] have been successfully used for the removal of pharmaceuticals in water. However, the studied catalytic ozonation processes (e.g. ozonation on metal oxides), despite providing high removal efficiency [9], tend to utilise radical mechanisms, which can be significantly hindered by radical scavengers [6,9]. Therefore, it is important to consider also catalytic process utilising more selective molecular ozone reactions, which are not affected by radical scavengers. In this work ZSM-5 zeolites have been used. To the authors' knowledge, this is the first report discussing the application of ZSM-5 zeolites for the removal of ibuprofen in water.

Carboxylic acids, stable ozonation by-products of other organic pollutants [21], are the third group of pollutants studied in this work. They are highly resistant to oxidation. Several catalysts have been used for the removal of organic acids [6]. However, these processes are not usually effective in the presence of hydroxyl radical scavengers [6]. In this work acetic acid has been selected as a target compound.

2. Experimental

2.1. Materials and reagents

The ZSM-5 zeolites used in this work were supplied by Zeochem (Switzerland). Ibuprofen, VOCs, humic acid and acetic acid were

obtained from Sigma–Aldrich. All chemicals used were of analytical grade and were used without further purification.

2.2. Ozonation experiments

The ozonation experiments were conducted at room temperature (20 °C) in a semi-continuous mode as shown in Figure S1 (column length, 70 cm; width, 31 mm; catalyst bed height, 5 cm). Aqueous solution (490 mL) spiked with organic pollutants (cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) or ibuprofen (20 mg/L) or acetic acid (20 mg/L) was transferred to the column containing 5 g of the catalyst, and was recirculated over the period of 30 min and a flow rate of 15 mL/min. Ozone was generated from pure oxygen by AZCO HTU-5000GE-120 ozone generator and was continuously introduced to the column by means of a ceramic sparger at a flow rate of 0.1 mg/min (in the case of VOCs ozonation) or 0.5 mg/min (in the case of ibuprofen and acetic acid ozonation). The samples were collected at 5 min intervals and were quenched with 0.025 M Na_2SO_3 in order to remove any residual ozone. All the samples were filtered (PTFE 0.45 μm syringe filter) prior to the analysis.

The possible loss of VOCs due to volatilisation was determined by recirculation of 490 mL of VOCs solution in the reaction column for 30 min. A saturated solution of VOCs was used in the ozonation experiments and was prepared by directly spiking VOCs to a flask containing 1 L of ultrapure water. The volumetric flask was shaken manually for 5 min and then was placed in a dark place for 24 h. After 24 h, 500 mL of saturated solution was pumped out from underneath the organic layer using Watson Marlow 323 pump.

The ozonation experiments in the presence of tertiary butyl alcohol (TBA), humic acid and phosphates were performed as

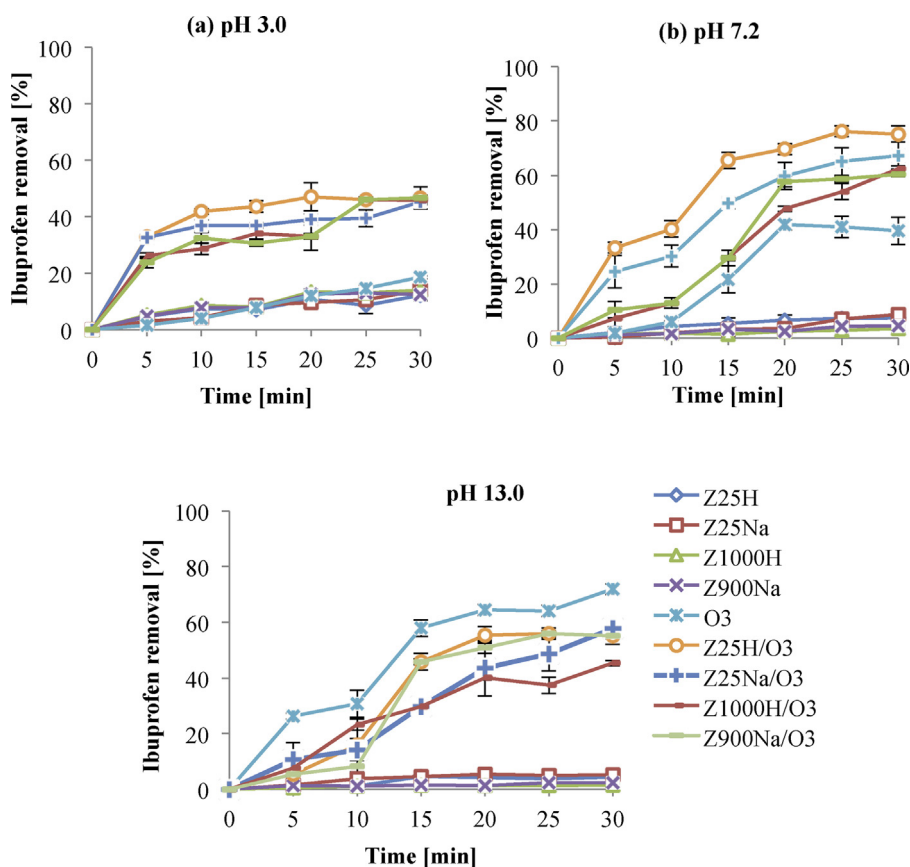


Fig. 1. Removal of ibuprofen by adsorption, ozonation alone and catalytic ozonation ($C_0(\text{ibu}) = 15$ mg/L; $O_3 = 0.5$ mg/min; $T = 20^\circ\text{C}$; pH = 3.0, 7.2 and 13.0; catalyst dose = 5.0 g; $V = 490$ mL).

described above by adding 50 mg/L of TBA or phosphates, or 7 mg/L of humic acid to the semi-continuous reactor following the above procedure. Furthermore, the removal of humic acid during catalytic ozonation was evaluated without the addition of ibuprofen and VOCs.

The reuse performance of catalyst in the removal of ibuprofen and VOCs was also investigated in the semi-continuous reactor (Figure S1) according to the above procedure. For this purpose 5 g of catalyst was added in 490 mL solution containing ibuprofen (20 mg/L). The ozonation time was fixed to 30 min. After every 30 min a fresh solution of pollutants was introduced in a semi-continuous reactor. The cycle was repeated 12 times.

2.3. Adsorption experiments

The adsorption experiments of selected pollutants such as VOCs (cumene, chlorobenzenes), ibuprofen and acetic acid were performed in the semi-continuous reactor. For this purpose 5.0 g

of the catalyst was added to 490 mL of saturated VOCs solution (cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) or ibuprofen (20 mg/L) or acetic acid (20 mg/L) solutions. The solutions were recirculated for 30 min (flow rate, 15 mL/min). The samples were collected after every 5 min and were filtered (PTFE 0.45 μ m syringe filter) prior to the analysis.

2.4. Analytical procedures

2.4.1. Ozone dose

The iodometric method [22] was used for the determination of ozone in the gas phase. Gaseous ozone in in-gas and off-gas was continuously introduced to two sets of glass bottles, each filled with 200 mL of 2% KI, through a ceramic sparger (Figure S1). After acidification of 200 mL of the 2% KI solution with 10 mL of 1 N HCl, the liberated iodine was titrated with standard 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$ using a starch indicator.

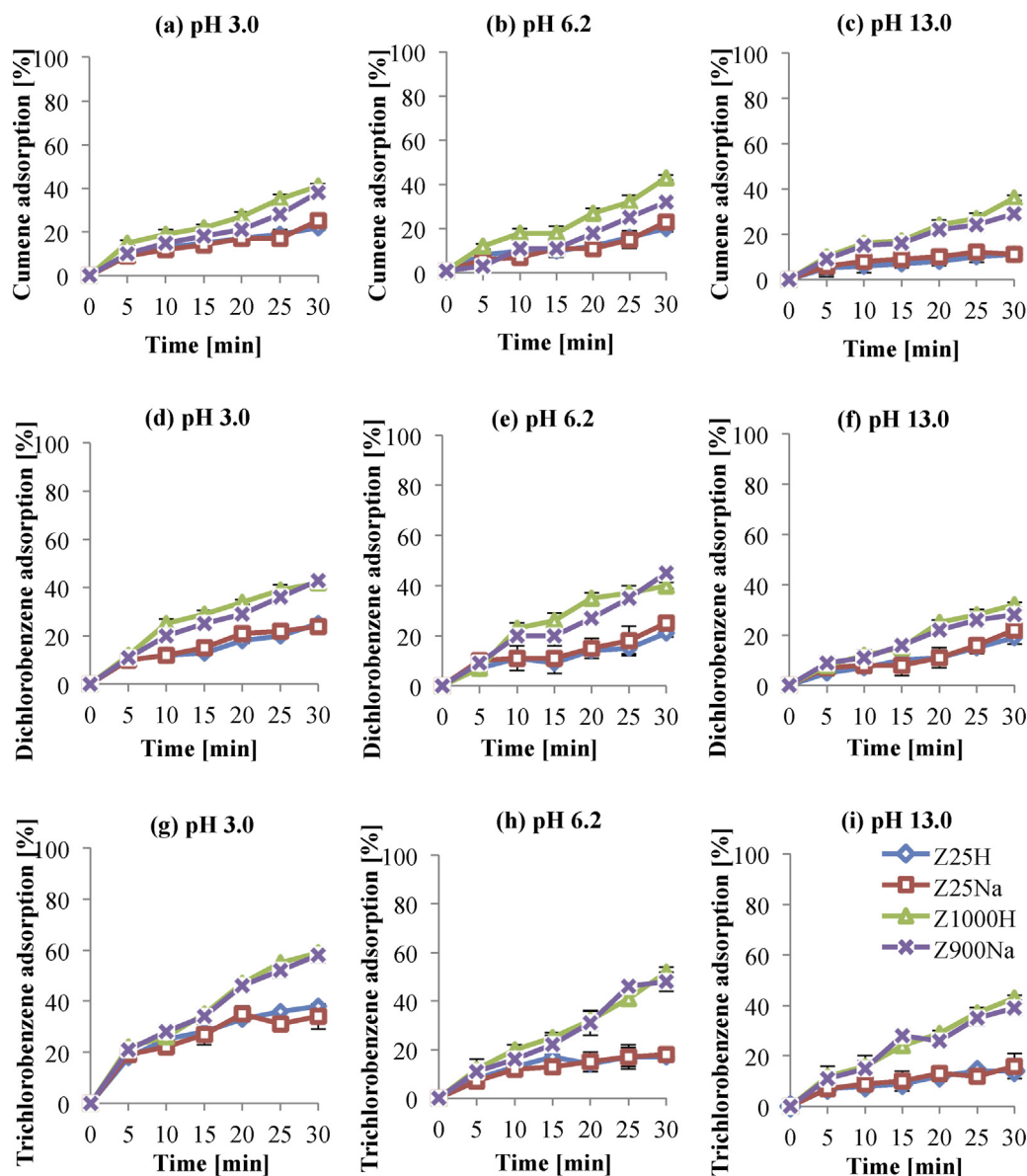


Fig. 2. Removal of VOCs by adsorption on ZSM-5 zeolites ($C_{0(\text{cum})} = 19.2$ mg/L; $C_{0(\text{DCB})} = 3.5$ mg/L, and $C_{0(\text{TCB})} = 0.5$ mg/L; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$; adsorbent dose = 5.0 g; $V = 490$ mL).

2.4.2. Aqueous ozone

The concentration of ozone dissolved in aqueous phase was determined by the indigo method [22]. The difference in absorption of light at 600 nm between blank and sample was measured with a Shimadzu UV-160 A UV–vis spectrophotometer. The calibration curve was established before analysis.

2.4.3. Analysis of VOCs

VOCs were determined by gas chromatography coupled with mass spectrophotometry (GC/MS, Agilent). After liquid–liquid extraction (hexane:water, 1:5; extraction time, 1 min) 1 μ L of the extractant solution was injected using an auto sampler and a split-less mode. The temperature programme used was as follows: 50 °C for 4 min then 50 °C/min to 200 °C. The carrier gas flow rate was 1.3 mL/min. The scan mode was selected in the mass range of 50–500 and mass transfer line temperature was 280 °C. The limits of quantification for cumene, dichlorobenzene and trichlorobenzene were 0.8 ppm, 0.5 ppm and 0.4 ppm respectively. The limits of

detection for cumene, dichlorobenzene and trichlorobenzene were 0.4 ppm, 0.3 ppm and 0.1 ppm respectively. The RSD was less than 5%.

2.4.4. Analysis of ibuprofen

Ibuprofen was analysed by Gilson 506C HPLC equipped with UV–visible detector and Phenomenex Kinetex 2.6 μ m C₁₈ 100 Å column (100 mm \times 4.60 mm). The injection volume was 30 μ L and the flow rate of mobile phase was of 0.4 mL/min. The mobile phase used was methanol/water (70:30, v/v) modified with 1% acetic acid (pH 3). The limits of detection and quantification were 0.2 ppm and 0.5 ppm respectively. The RSD was less than 5%.

2.4.5. Analysis of organic acids

Organic acids were analysed with the use of Dionex DX-120 ion chromatograph, equipped with Ion Pac-ICE-ASI 9 mm \times 250 mm column and AMMS-TCE 300 anion micro membrane suppressor. Heptafluorobutyric acid (1.0 mM) was used as eluent and

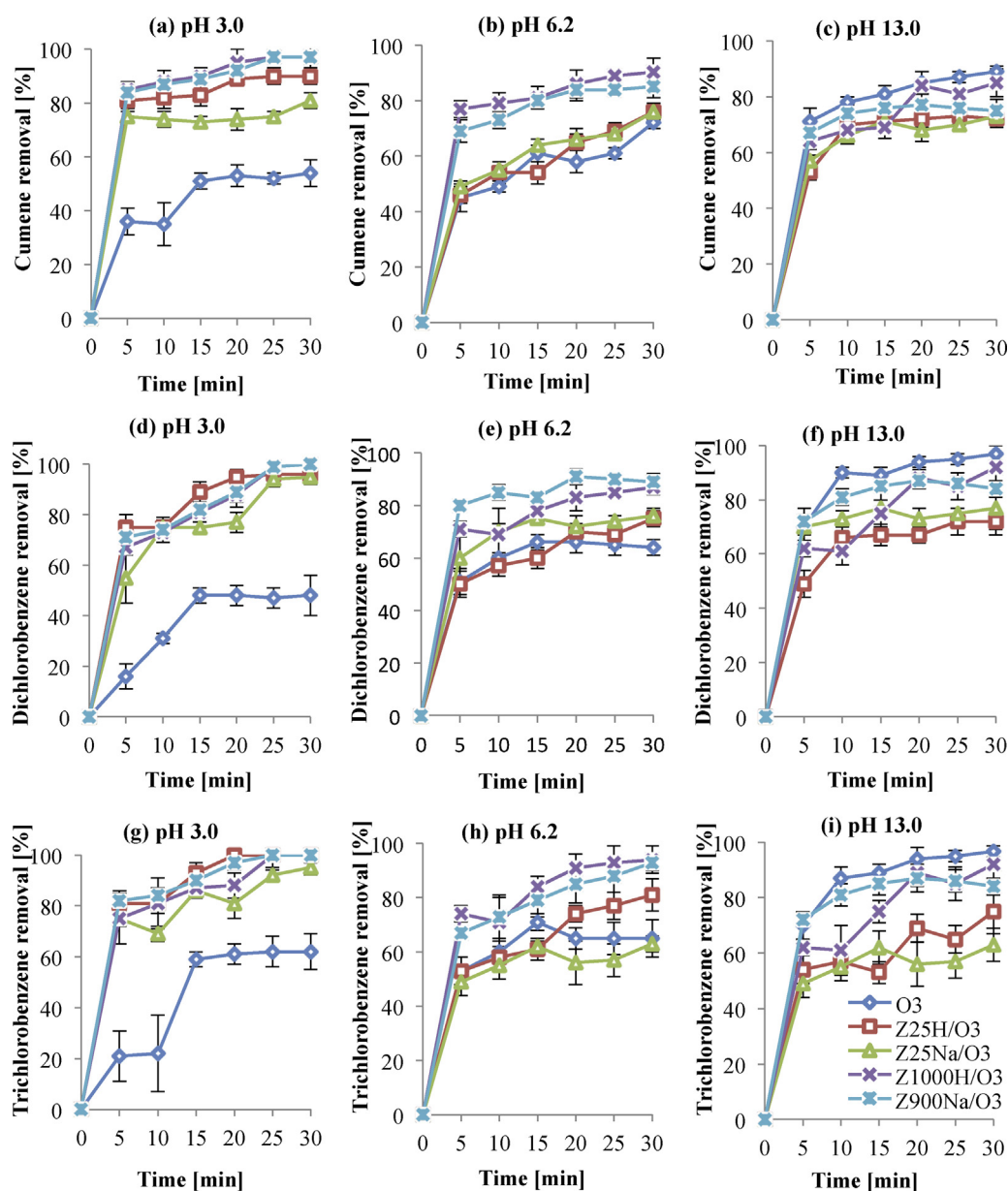


Fig. 3. Effect of pH on VOCs removal by ozonation alone and ozonation in the presence of ZSM-5 zeolites ($C_{0(\text{cum})} = 19.2$ mg/L, $C_{0(\text{DCB})} = 3.5$ mg/L, and $C_{0(\text{TCB})} = 0.5$ mg/L; $T = 20$ °C; pH = 3.0, 6.2 and 13.0; pH_{30min} = pH₀ \pm 0.3; catalyst amount = 5 g; V = 490 mL; O₃ = 0.1 mg/min).

tetrabutylammonium hydroxide (5 mM) was used as regenerant. The injection volume was 25 μ L, cell temperature was 30 °C and eluent flow and regenerant rate were 0.82 mL/min and 5 mL/min respectively. The limits of detection and quantification for acetic acid were 0.3 ppm and 0.5 ppm respectively. The RSD was less than 5%.

2.4.6. Analysis of phosphates

Phosphate concentrations were determined by ion chromatography using a DIONEX DX-120 system with Ion Pac As14 analytical column (4 mm \times 250 mm) and Ion Pac AG14 guard column (4 mm \times 250 mm) coupled to an ED-50A electrochemical detector (Dionex, USA). Analyses were performed using an isocratic method at a flow rate of 0.82 mL/min and a constant temperature of 30 °C. The mobile phase consisted of 3.5 mM sodium carbonate and 1.0 mM sodium hydrogen carbonate. The injection volume of sample was 25 μ L. The limits of detection and quantification for phosphates were 0.3 ppm and 0.6 ppm respectively. The RSD was less than 5%.

2.4.7. Analysis of humic acid

Humic acid concentration was determined through the measurement of absorbance at 254 nm with the usage of Shimadzu UV-160A UV-Vis spectrophotometer. The sample was filtered and was placed in a 1.0 cm quartz cell. The calibration curve was established before analysis. The limits of detection and quantification were 0.5 ppm and 0.9 ppm respectively. The RSD was less than 5%.

3. Results and discussion

3.1. Catalytic ozonation of pharmaceuticals, VOCs and carboxylic acids on zeolites

3.1.1. Catalytic ozonation of ibuprofen and formation of by-products

The results presented in Fig. 1 indicate that ibuprofen shows higher adsorption on zeolites at pH 3 than at pH 7.2 and 13. Furthermore, adsorption capacity is zeolite dependant, with zeolites characterised by high SiO₂/Al₂O₃ ratios (Z1000 and Z900) showing the highest adsorption capacity at acidic pH and zeolites characterised by low SiO₂/Al₂O₃ ratios (Z25) showing the highest adsorption capacity at neutral and basic pH. For example 0.6 mg of ibuprofen was sorbed on 1 g of Z25H within 30 min at pH 3.0 and only 0.16 mg of ibuprofen was sorbed on 1 g of Z25H at pH 13.0. This is because ibuprofen is protonated at pH 3 (pK_a of ibuprofen is 4.9), which facilitates hydrophobic interactions. At pH 7.2 and 13, ibuprofen is negatively charged, which results in weaker interactions with zeolites. Low adsorption of ibuprofen at pH 13 may be due to the influence of hydroxide ions, since the surface of the catalyst is fully populated with hydroxide ions at this pH.

The results presented in Fig. 1 show that catalytic ozonation on ZSM-5 zeolites was effective at pH 3 and 7.2, with the highest activity observed in the case of Z25 zeolites. However, zeolites did not show any activity at a basic pH of 13. This may be due to the high concentration of OH[−] ions that are responsible for high rates of aqueous ozone decomposition at pH 13 [23]. Indeed, aqueous ozone concentrations were found to be very low at pH 13 during both catalytic ozonation and ozonation alone (Figure S2). As a result,

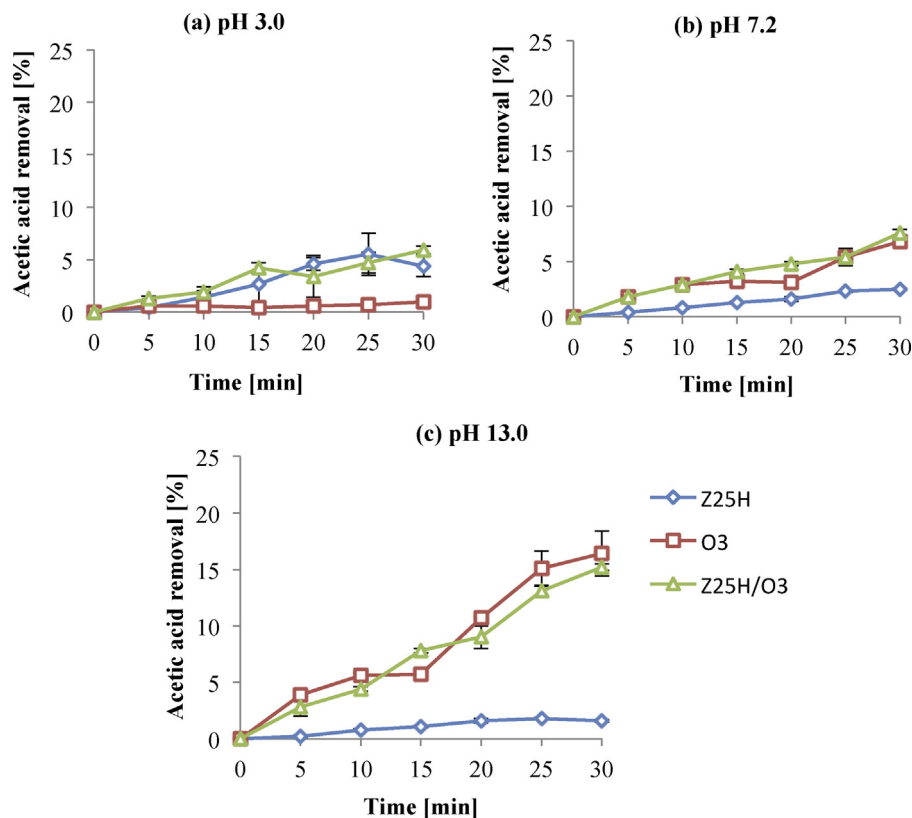


Fig. 4. Removal of acetic acid by adsorption, ozonation alone and catalytic ozonation ($C_{0(\text{ace})} = 15$ mg/L; $O_3 = 0.5$ mg/min; $T = 20$ °C; pH = 3.0, 7.2 and 13.0; Catalyst dose = 5.0 g; $V = 490$ mL).

any reaction of ibuprofen with ozone on the surface of the catalysts would be unlikely.

Furthermore, the results indicate that the catalytic activity of ZSM-5 zeolites towards ibuprofen increases with the decrease of pH and is the highest at pH 3.0. For example, at pH 3.0 the removal of ibuprofen in the presence of zeolites was 28% (Fig. 1) higher than that of ozonation alone (after 30 min ozonation time) and only 22% higher at pH 7.2. This may be due to the high adsorption of ibuprofen on zeolites at pH 3. Additionally, ozone is more stable at low pH (Figure S2), which facilitates molecular ozone reactions on zeolites. Similar results have been reported in the case of coumarin and NBD-Cl removal on zeolites [9,24]. Enhanced oxidation of ibuprofen during catalytic ozonation at pH 3 can also be confirmed by the formation of carboxylic acids (acetic, formic and succinic acid; Figure S3), which are stable ozonation by-products. It is worth emphasising that ozonation alone did not lead to the formation of carboxylic acids at detectable levels. Formation of carboxylic acids during catalytic ozonation as opposed to ozonation alone is indeed an indication of extensive oxidative processes occurring. Furthermore, acidic by-products have not been observed at pH 7.2 and

13.0. This may be because of hydroxide ions in solution which can decompose aqueous ozone and as a result generate hydroxyl radicals that can degrade organic acids. It is important to indicate that at low pH the removal of ibuprofen in the case of catalytic ozonation is higher when compared with the sum of ozonation alone and adsorption. However, at higher pH (pH 13) catalytic ozonation is not a dominant mechanism. This is because ozone is less stable at higher pH values and zeolites require ozone to adsorb on their surface in order to achieve an effective catalytic oxidation process.

3.1.2. Catalytic ozonation of VOCs and formation of by-products

Ozone reacts with aromatic compounds with the formation of ozonide and finally the destruction of aromatic ring leading to the production of by-products such as aldehydes, ketones and organic acids [25]. The ozonation reactions of a wide range of organic compounds including aromatic compounds of different functionalities including aldehydes, ketones, carboxylic acids and halogens have been studied previously [26]. In this paper

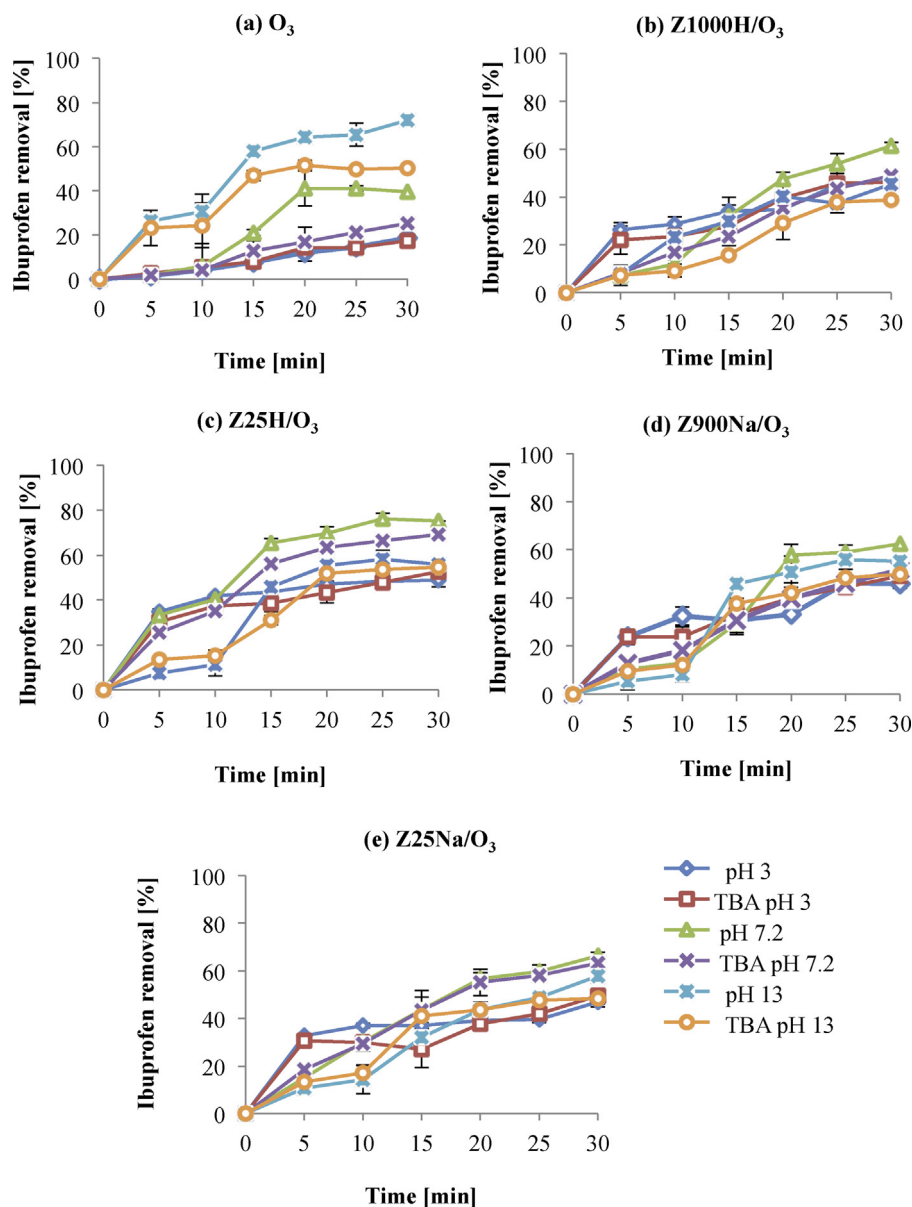


Fig. 5. Effect of TBA on ozonation alone and ZSM-5/O₃ ($C_{0(\text{ibu})}$ = 15 mg/L; T = 20 °C; pH = 3.0, 7.2 and 13.0; T = 30 min; O_3 = 0.5 mg/min; TBA = 50 mg/L; V = 490 mL).

catalytic ozonation on zeolites was undertaken to remove VOCs from water.

The results presented in Fig. 2 show that much higher quantities of cumene, dichlorobenzene and trichlorobenzene were adsorbed on Z1000H and Z900Na when compared with Z25H and Z25Na. This may be due to higher hydrophobicity of Z1000H and Z900Na. The results at different pH values revealed lower affinity of VOCs towards zeolites at pH 13. As discussed earlier this is because the surface of catalysts is populated at this pH with hydroxide ions. Similar results have been obtained in the case of coumarin adsorption studies [9]. The results further revealed that the pH value of solution has a significant effect on adsorption of chlorobenzenes. An increase in adsorption was observed with a decrease in the pH of the solution. This effect was more pronounced in the case of trichlorobenzene. For example, adsorption of trichlorobenzene on Z1000H was 55% (0.3 mg/g) at pH 3 and only 45% (0.2 mg/g) at pH 6.2. On the other hand adsorption of cumene on the studied catalysts was not significantly pH dependant.

The comparative study between VOCs and ibuprofen adsorption further revealed that silica to alumina ratios of zeolites and the nature of pollutants are important parameters in the adsorption of pollutants. Z25H and Z25Na showed the highest adsorption of ibuprofen in its ionised form (Fig. 1). On the other hand, Z1000H and Z900Na showed the highest adsorption of VOCs at all pH values (Fig. 2).

The catalytic ozonation of VOCs on zeolites was investigated at pH values 3.0, 6.2 and 13.0. The results presented in Fig. 3

indicate that as the pH of the solution increases, the difference in VOCs removal percentage in ozonation alone and ozonation in the presence of ZSM-5 zeolites decreases. For example, the difference in the removal of VOCs between Z1000H/O₃ and O₃ at pH 3 was 43% and it decreased to only 14% at pH 6.2. This clearly suggests that the activity of ZSM-5 zeolites increases with the decrease of pH. At pH 13 zeolites are not effective. Similar results have been obtained in the case of ibuprofen (Fig. 1). These results are also supported by the work of Amin et al. [10] who suggested that zeolites are more active at acidic pH. This may be because, as discussed above, aqueous ozone is more stable at acidic pH (Figure S4). Furthermore, the results indicated that zeolites with high silica content show better activity, which is due to the higher adsorption of VOCs on more hydrophobic ZSM-5 zeolites. Additionally, it is worth emphasising here that catalytic activity is clearly visible at pH 3.0 (the removal of VOCs during catalytic ozonation is higher than the sum of ozonation alone and adsorption). This is because ozone is more stable at low pH.

The above results indicate that high silica zeolites are both good adsorbents of studied organic contaminants and good catalysts of ozonation. The observed rapid decrease in VOCs concentrations during the first 5 min of ozonation time in the presence of ZSM-5 may be due to the rapid adsorption of VOCs on the catalyst surface. However, it should be emphasised that the comparison of all studied processes: adsorption, ozonation and catalytic ozonation revealed that the removal of cumene at pH 3 (in the first 5 min) was on average 10% higher in the case of catalytic ozonation when

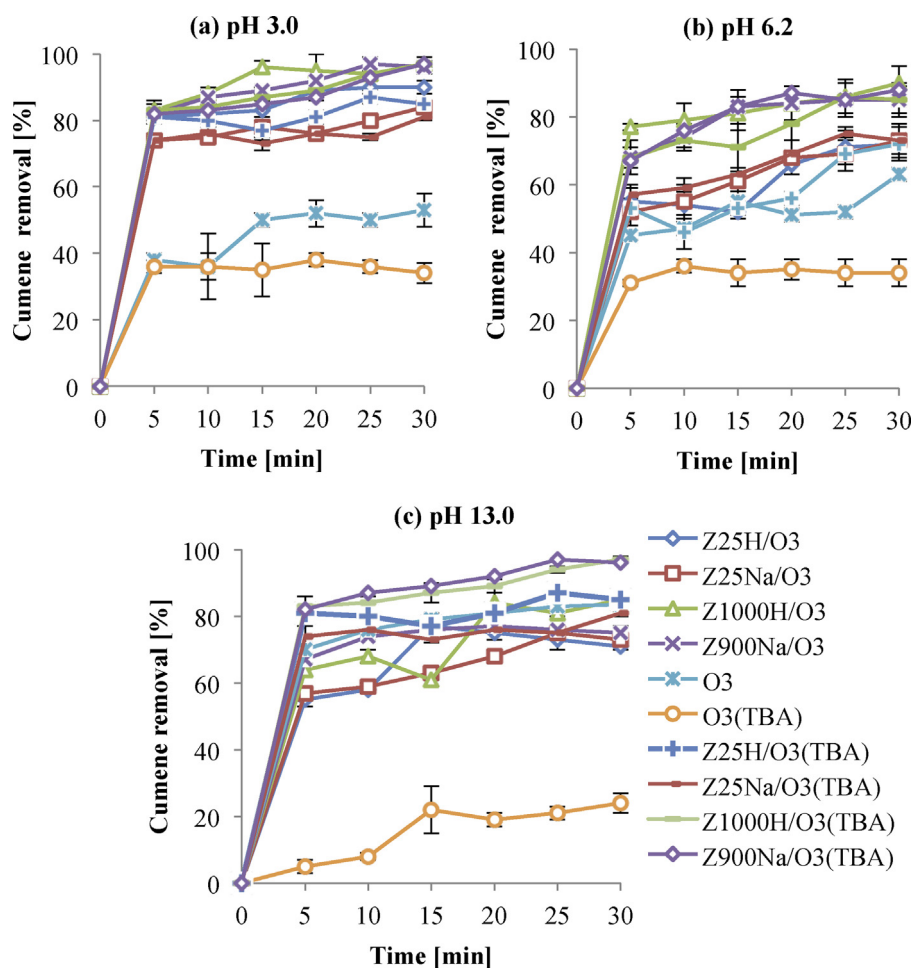


Fig. 6. Effect of TBA on cumene removal by O₃ and ZSM-5/O₃ ($C_{0(\text{cum})}$ = 19.2 mg/L; T = 20 °C; pH = 3.0, 6.2 and 13.0; $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$; TBA = 50 mg/L; V = 490 mL; O_3 = 0.1 mg/min).

compared to combined ozonation alone and adsorption. This clearly suggests that ZSM-5 zeolites catalyse VOCs removal. Formation of carboxylic acids (acetic, formic and succinic acids) during catalytic ozonation of VOCs (Figure S5), which was observed only at pH 3, is yet more evidence for enhanced oxidation processes occurring and leading to the removal of VOCs. Similarly to ozonation of ibuprofen, ozonation alone did not lead to the formation of carboxylic acids at detectable levels. Furthermore, acidic by-products were not observed at pH 7.2 and 13.0. This may be because of hydroxide ions in solution which can decompose aqueous ozone and as a result generate hydroxyl radicals that can degrade organic acids.

It is interesting to note here that among VOCs, cumene was removed to the greatest extent when compared with chlorobenzenes. This may be due to the structure of compounds. Cumene contains aromatic ring activating group. However, chlorobenzenes have electron donating groups, and therefore they are highly resistant to ozone attack.

It is also important to note that no significant change in the pH of solution was observed in all experiments after 30 min reaction time.

3.1.3. Catalytic ozonation of acetic acid

It is well known that the reactions of ozone with organic compounds lead to the formation of by-products and among them the most common are aldehydes, ketones and carboxylic acids [24]. Carboxylic acids are the most stable ozonation by products. The short chain organic acids tend to accumulate in solutions due to their low reactivity with ozone. As a result, ozonation alone is not

sufficient for their effective degradation [1]. In this study, carboxylic acids were also found, as discussed above, to be formed during catalytic ozonation of both ibuprofen and VOCs. It was therefore decided to study their removal during catalytic ozonation. Acetic acid was chosen as a target compound. Z25H was chosen as a catalyst for ozonation experiments.

The results presented in Fig. 4 indicate the percentage adsorption of acetic acid on Z25H. The process was found to be pH dependent and adsorption of acetic acid was found to increase with the decrease of pH. For example percentage adsorption of acetic acid was 4% (0.6 mg/g) at pH 3 after 30 min and was reduced to 1% (0.1 mg/g) at pH 13.0. It is interesting to note here that acetic acid is ionised at basic pH ($pK_a = 4.7$). Therefore, similarly to ibuprofen, it was found to have the highest adsorption in its protonated form, which is at acidic pH.

The results presented in Fig. 4 show that the removal of acetic acid increases with an increase in pH in the case of ozonation alone and is the highest at pH 13 (15%). The results further revealed that at pH 13 Z25H does not show any catalytic activity in the removal of acetic acid when compared with ozonation alone. Low catalytic activity was observed, similarly to ibuprofen degradation, at pH 3.0, which is when acetic acid is protonated as shows some adsorption on zeolites. Aqueous ozone decay during ozonation alone and catalytic ozonation is presented in Figure S6. These results further support our hypothesis that ZSM-5 zeolites do not decompose aqueous ozone leading to the formation of active oxygen species [9] and they mainly operate through the adsorption mechanism, in which both the pollutant and ozone adsorb on the surface of

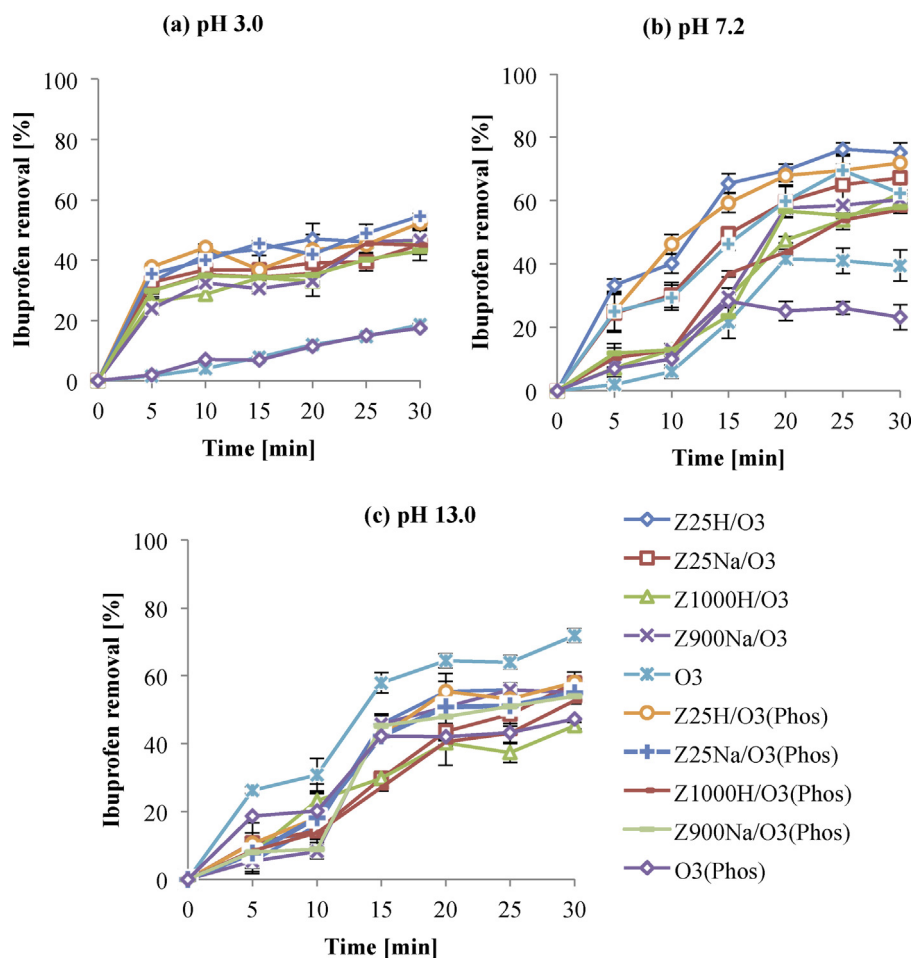


Fig. 7. Effect of phosphates on ibuprofen removal by O_3 and ZSM-5/ O_3 ($C_{0(\text{ibu})} = 15 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 7.2$ and 13.0 ; $t = 30 \text{ min}$; $O_3 = 0.5 \text{ mg/L}$; phosphates = 50 mg/L ; $V = 490 \text{ mL}$).

catalysts with their subsequent reactions on the surface. Since acetic acid is highly resistant to direct ozone attack the reactions of direct ozone with adsorbed acetic acid are potentially very slow. It is important to indicate here that catalytic ozonation does not cause any significant increase in the removal efficiency of acetic acid at any studied pH values. This may be because acetic acid is refractory to ozone, which further supports our hypothesis that zeolites catalyse oxidation processes by facilitating direct reactions of molecular ozone with pollutants.

3.2. Mechanisms of catalytic ozonation

3.2.1. Effect of tert-butyl alcohol on the efficiency of catalytic ozonation on ZSM-5

The effect of tertiary butyl alcohol (TBA) on catalytic ozonation at different pH values has been investigated in order to understand the mechanism of ibuprofen and cumene removal by ZSM-5 zeolites. It has already been reported that zeolites do not decompose ozone to generate hydroxyl radicals [9]. In this study the formation of radicals in the presence of ibuprofen and VOCs was investigated.

The results presented in Figs. 5 and 6 show that TBA decreases the efficiency of ibuprofen and cumene removal during ozonation alone, which indicates that hydroxyl radicals are formed during ozonation alone and play an active role in the decomposition process. The highest decrease in ozonation efficiency was observed at basic pH, which was to be expected due to high ozone decomposition rates and formation of hydroxyl radicals at basic pH.

Interestingly, TBA did not have any significant effect on the catalytic ozonation of ibuprofen and VOCs under the investigated pH conditions in the presence of all four ZSM-5 zeolites (Figs. 5 and 6). The highest difference (although still minimal) in the removal of ibuprofen with and without TBA at pH13 (Fig. 5) is attributed to the presence of small quantities of hydroxyl radicals formed in the bulk solution as a result of the interaction of hydroxide ions with ozone.

The general lack of measurable effects of TBA on ozonation efficiency of ibuprofen and VOCs during catalytic ozonation is an indication that hydroxyl radicals are not the dominant active species in the ZSM-5/O₃ process. This suggests that zeolites do not decompose aqueous ozone leading to the production of hydroxyl radicals. The results further indicate that within the family of zeolites the nature of counter ions does not have a significant effect on the mechanism of the process.

3.2.2. Effect of phosphates on the efficiency of catalytic ozonation on ZSM-5

The inorganic ions such as phosphates, sulfates, carbonates and bicarbonates are commonly present in drinking waters. These ions are known as hydroxyl radical scavengers. Additionally, they may adsorb on the catalyst surface and poison it [9]. The influence of phosphates in the presence of ZSM-5 zeolites has been previously studied [9]. It has been observed that phosphates do not have a significant effect on catalytic process in the presence of zeolites [9]. This study may further help to understand the influence of

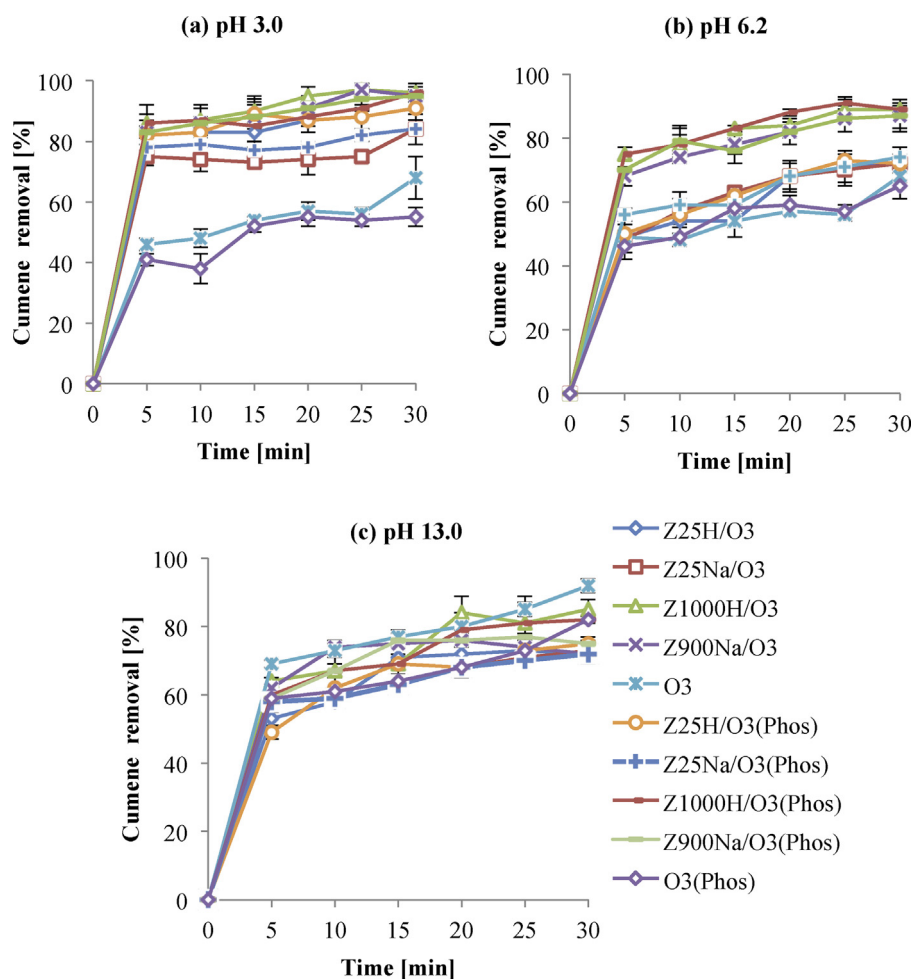


Fig. 8. Effect of phosphates on cumene removal by O₃ and ZSM-5/O₃ ($C_{0(\text{cum})}$ = 19.5 mg/L; T = 20 °C; pH = 3.0, 6.2 and 13.0; t = 30 min; O₃ = 0.1 mg/L; phosphates = 50 mg/L; V = 490 mL).

phosphates on the removal of different pollutants in the presence of zeolites.

The adsorption results indicate that ZSM-5 zeolites have a low adsorption capacity (<4%) towards phosphates (Figure S7), which decreases with the increase of pH. Such a phenomenon results from the presence of hydroxide ions that can suppress the adsorption of phosphates due to the fact that hydroxide ions are stronger bases. It is worth emphasising that, as expected, Z25 zeolites with higher alumina content have slightly better adsorption capacity towards phosphates (Figure S7). Due to limited sorption of phosphates on zeolites the presence of phosphates in water did not have a significant effect on the catalytic activity of all zeolites during ozonation of ibuprofen and VOCs (Figs. 7 and 8). This is a very important finding indicating that ionic natural water constituents such as phosphates will not act as interferences of ozonation process and will not poison the catalyst as is the case with catalytic ozonation on alumina [9].

3.2.3. Effect of humic acids on the efficiency of catalytic ozonation on ZSM-5

Humic acids are an important component of natural organic matter and they are widely present in natural waters. It is therefore of importance to study the possible effects of humic substances on the efficiency of catalytic ozonation. In this work, the effect of humic acid was studied in the catalytic ozonation of ibuprofen and VOCs (cumene).

The results presented in Figs. 9 and 10 clearly indicate that humic substances did not have any significant effect on ibuprofen and cumene removal. It is worth emphasising that this effect was particularly low in the case of high silica zeolites. This is because, similarly to phosphates, the studied ZSM-5 zeolites show low adsorption capacity towards humic acids (0.3 mg/g) (Figure S8). Furthermore, humic acid was found not to be degraded to a high extent during both ozonation alone and catalytic ozonation (the UV_{254} absorbance decrease was <20% at pH 7.2 (Figure S8). No catalytic activity of studied zeolites was therefore observed in the case of humic acids.

3.2.4. Effect of drinking water constituents on the efficiency of catalytic ozonation on ZSM-5

In order to verify the possible effects natural water constituents might have on catalytic ozonation efficiency, the catalytic activity of zeolites (Z1000H and Z25H) during ozonation of ibuprofen and VOCs was also investigated in drinking water. The results are presented in Fig. 11. Z1000H and Z25H have been selected for VOCs and ibuprofen removal respectively, as they showed the highest activity towards these compounds. As expected, no decrease in the catalytic activity of studied zeolites was observed in drinking water when compared to deionised water. This is because, as described above, the ZSM-5 zeolites do not promote the formation of hydroxyl radicals [9] and the adsorption of inorganic ions and humic substances is very low [9]. Hence the removal of VOCs and ibuprofen

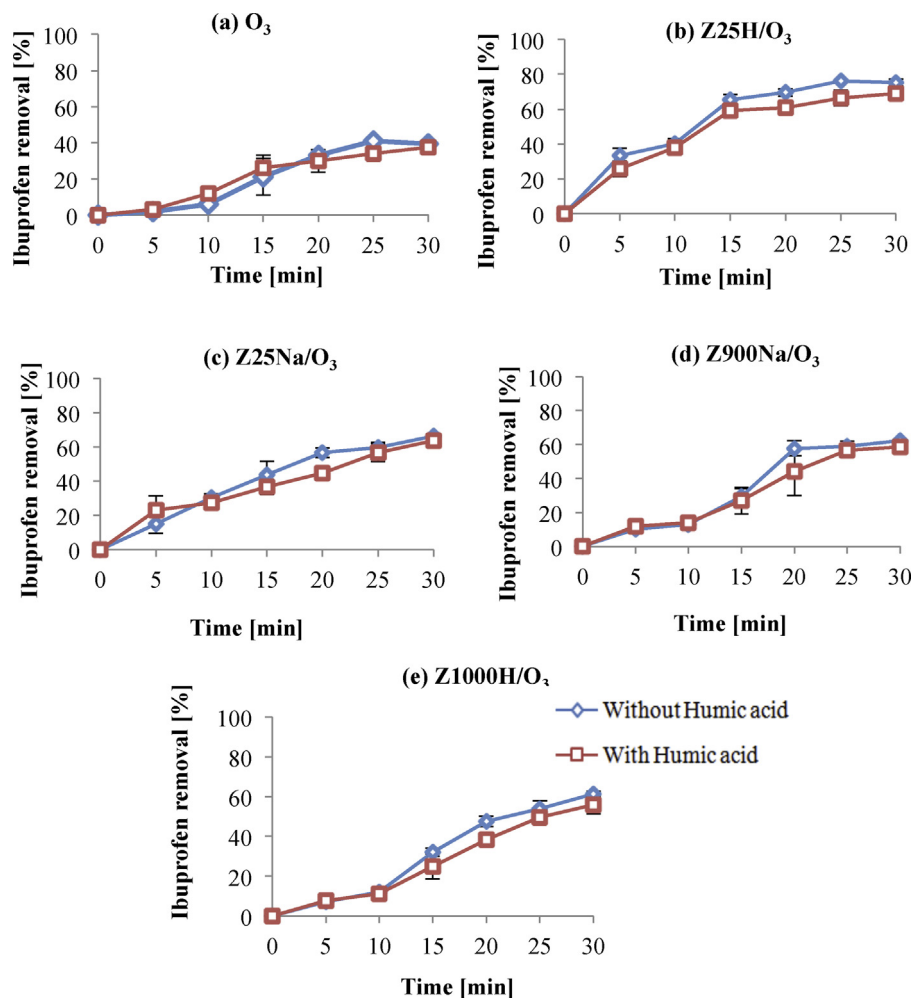


Fig. 9. The effect of humic acid on the removal of ibuprofen by ozonation and ozonation in the presence of ZSM-5 zeolites ($C_{0(\text{ibu})} = 15 \text{ mg/L}$; $C_{0(\text{HA})} = 7.0 \text{ mg/L}$; $T = 20^\circ\text{C}$; $O_3 = 0.5 \text{ mg/L}$; $\text{pH} = 7.2$; catalyst = 5.0 g ; $V = 490 \text{ mL}$).

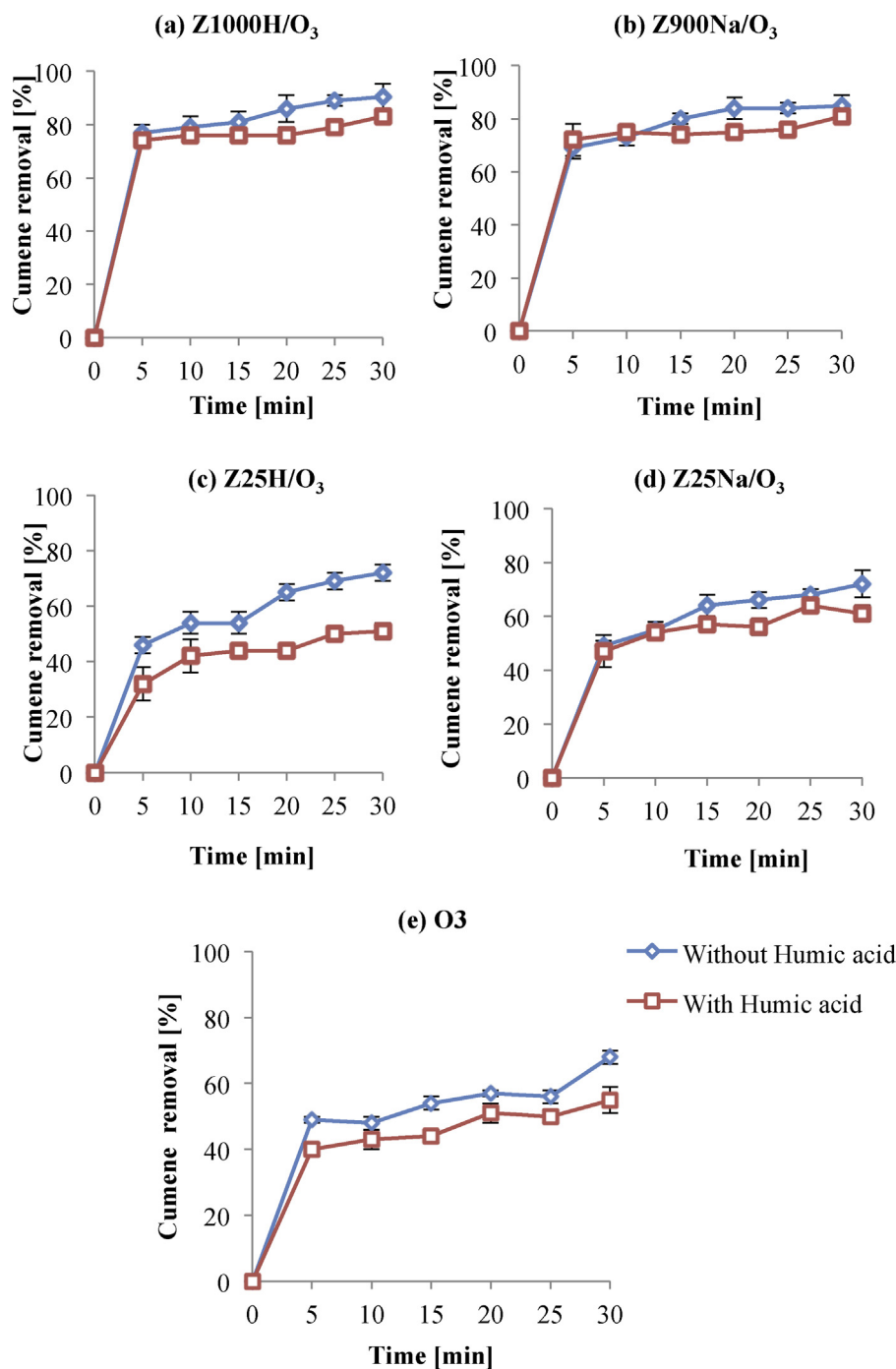


Fig. 10. Effect of humic acid on cumene removal by O₃, and ZSM-5/O₃ ($C_{0(\text{cum})} = 19.2 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{pH} = 6$; $\text{pH}_{30 \text{ min}} = \text{pH}_0 \pm 0.2$; humic acid = 7.0 mg/L ; catalyst amount, 5.0 g ; $V = 490 \text{ mL}$, $\text{O}_3 = 0.1 \text{ mg/min}$; $\lambda_{\text{max}} = 224 \text{ nm}$).

is not affected by natural water constituents. It is also important to mention that no significant change of pH ($\text{pH} \pm 0.05$) was observed during both ozonation and catalytic ozonation experiments.

3.2.5. Proposed mechanism

The results presented in this work indicate that catalytic ozonation on ZSM-5 zeolites proceeds via initial adsorption of both the pollutants and ozone on the surface of zeolites and is followed by their subsequent reactions, which result in the degradation of pollutants and the formation of oxidation by-products such as organic acids (Fig. 10). Molecular ozone reactions are particularly evident at acidic pH. At higher pH values both molecular ozone and

hydroxyl radicals (in the bulk solution) contribute to the removal of studied pollutants. The mechanism presented in previous reports [9,24] clearly suggested that zeolites do not promote the formation of hydroxyl radicals, superoxide ions and hydrogen peroxide; the TBA results presented in this work provided yet another confirmation. Additionally, the work presented by Amin et al. [10] further supports this hypothesis. Also Fujita et al. [27] reported that ZSM-5 zeolites can adsorb ozone on their surface from aqueous solutions. Within the family of zeolites the silica to alumina ratio plays a significant role as observed during the catalytic ozonation experiments of VOCs and ibuprofen. The results of acetic acid removal further support the postulate that zeolites operate through

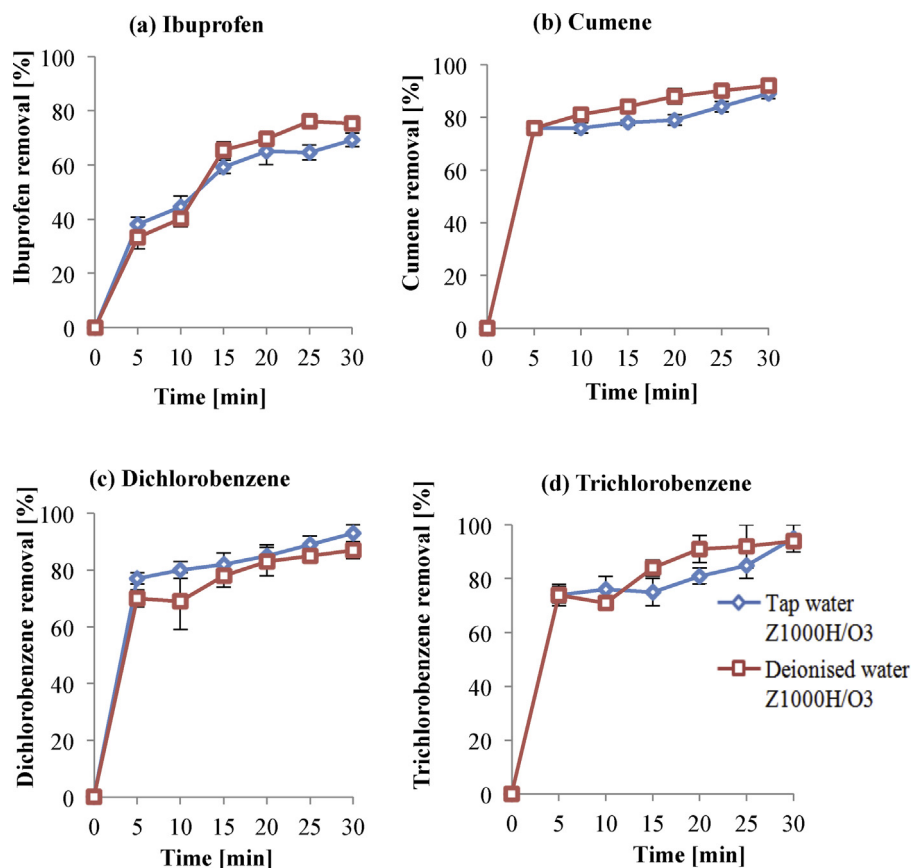


Fig. 11. Removal of VOCs and ibuprofen by Z1000H/O₃ and Z225H/O₃ in tap and deionised water ($C_{o(ibuprofen)} = 20$ mg/L, $C_{o(cumene)} = 19.2$ mg/L, $C_{o(DCB)} = 3.5$ mg/L and $C_{o(TCB)} = 0.5$ mg/L; $T = 20$ °C; $pH_{tap} = 7.3$, $pH_{deion} = 7.2$; $pH_{30min} = pH_0 \pm 0.2$; catalyst amount = 5 g; $V = 490$ mL; O₃ = 0.1 mg/min and 0.5 mg/min for VOCs and ibuprofen respectively).

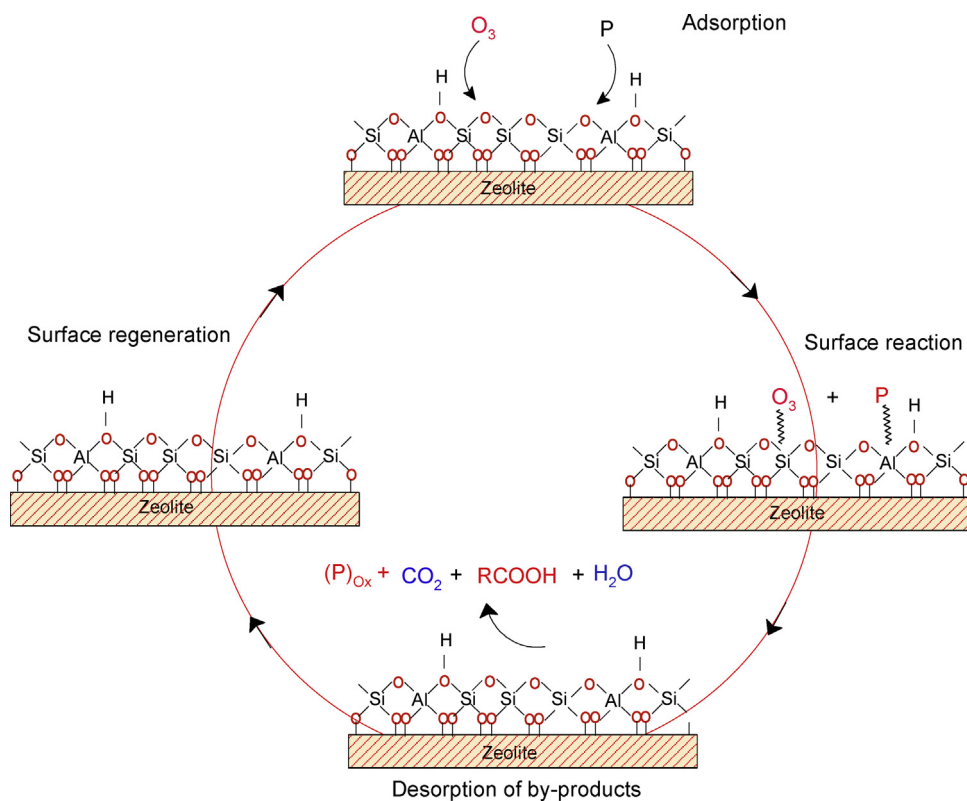


Fig. 12. Proposed mechanism of catalytic ozonation on ZSM-5 zeolites (P, Pollutants).

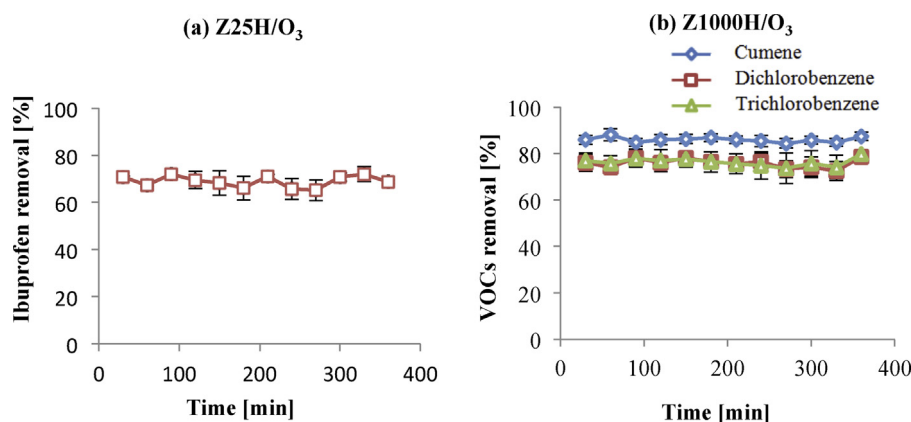


Fig. 13. Reuse performance experiments for removal of ibuprofen and VOCs by ZSM-5/O₃ ($C_{o(\text{ibu})} = 15 \text{ mg/L}$, $C_{o(\text{cum})} = 19.2 \text{ mg/L}$, $C_{o(\text{DCB})} = 3.5 \text{ mg/L}$ and $C_{o(\text{TCB})} = 0.5 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{O}_3 = 30 \text{ mg/L}$; $\text{pH} = 7.2$; catalyst = 5.0 g ; $V = 490 \text{ mL}$).

molecular ozone reactions on their surface. Since acetic acid is highly resistant to direct ozone attack the reactions of direct ozone with adsorbed acetic acid are potentially very slow Fig. 12.

3.3. The reuse performance experiments

Z25H and Z1000H have been selected to study the long-term performance of the ozonation of ibuprofen and VOCs respectively. The results presented in Fig. 13 show that the catalytic activity of Z25H and Z1000H does not change even after >300 min ozonation time. Thus the results indicate the considerable potential for practical application in water treatment. Furthermore, the reuse performance experiment provides further evidence that ozonation on zeolites is not just simply a combination of two independent processes of adsorption and ozonation occurring but a genuine catalytic process. Additionally, the adsorption capacities of zeolites for VOCs and ibuprofen have been determined and it has been observed that zeolites reached their maximum adsorption capacity within 30 min and 1 h in the case of VOCs and ibuprofen respectively. The continued constant removal of VOCs and ibuprofen beyond this time further suggested that a genuine catalytic process plays a key role in the removal of studied target pollutants from water.

4. Conclusions

The overall conclusions of this work are as follows:

1. ZSM-5 zeolites are effective, especially at acidic pH, in the catalytic ozonation of VOCs and ibuprofen; however they are ineffective in the removal of acetic acid. Their activity depends on their ability to adsorb pollutants which is directly related to silica to alumina ratios and hydrophobic–hydrophilic nature of pollutants.
2. The catalytic ozonation on zeolites proceeds via direct reaction of molecular ozone with pollutants. The presence of TBA was found to have no effect on the catalytic activity of zeolites.
3. The catalytic effect in ZSM-5 zeolites is due to their ability to promote surface reactions between the adsorbed ozone and pollutants and is independent of the nature of counter ions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.02.010>.

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